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Solvent Effects on Simple Electron Transfer Reactions.

A Comparison of Results in Debye and Non Debye Solvents

by

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Prepared for Publication

in

Journal of Electroanalytical Chemistry

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May 20, 1991

91-02544

REPORT DOCUMENTATION PAGE

May 20, 1991   Technical

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A Comparison of Results in Debye and Non Debye Solvents.   N00014-90-J-1235

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No. 10

Office of Naval Research
800 N. Quincy
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Prepared for publication in Journal of Electroanalytical Chemistry

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS	15. NUMBER OF PAGES
Electron Transfer, Non Debye Solvents, Dielectric Relaxation	18
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	

IN ALL CORRESPONDENCE
CONCERNING THIS PAPER
REFER TO:

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The title contains two separate phrases. This should be indicated with the appropriate break.

Solvent effects on simple electron transfer reactions: A comparison of results in Debye and non-Debye solvents

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(Received 13 August 1990; in revised form 16 October 1990)

Abstract

Estimation of the longitudinal relaxation time τ_L for non-Debye solvents is considered on the basis of Hynes' theory for solvents exhibiting more than one relaxation process. It is shown that the major portion of the solvent effect on electron transfer kinetics in these solvents follows that in Debye solvents when the high frequency limiting value is used for τ_L. The solvent effect on the outer sphere contribution to the Gibbs energy of activation is then examined with respect to the variation in solvent permittivity. Analysis of the available data suggests that the reactants involved in electron transfer are solvated mainly by solvent monomers such that the dielectric constant in the vicinity of the reactant considerably reduced in protic solvents.

INTRODUCTION

Our recent discussion of solvent effects on electron transfer reactions has focussed on data obtained in aprotic solvents [1–3]. These solvents are the simplest type of dipolar liquids, their dynamic dielectric properties often being described by the classical Debye model [4]. Studies of the effect of the solvent on the kinetics of heterogeneous electron transfer involving organic molecules showed a clear difference between the behaviour of aprotic solvents and protic solvents such as the alcohols and protic amides [5,6]. In the case of the electrooxidation of phenathiazene, Opallo and Kapturkiewicz [5] observed two linear correlations between the logarithm of the standard rate constant and the logarithm of the solvent's longitudinal relaxation time, one relationship being valid for aprotic solvents and the second, for protic ones. McManis et al. [7] studied the redox behaviour of metallocenes at a mercury electrode, and found that the standard rate constants in low molar mass alcohols were anomalously high with respect to those observed in aprotic solvents. Similar conclusions were reached with respect to data for homogeneous electron transfer involving cobaltacene and related metallocene systems [8].

It came 2 days earlier than expected.

Simple Debye solvents are characterized by a static permittivity ϵ_s, a high frequency value. ϵ_∞, and a characteristic relaxation time for rotational diffusion, τ_D. When the in- and out-of-phase components of the permittivity are measured as a function of the frequency of the electrical field applied to the liquid, a plot of the out-of-phase component ϵ'' against the in-phase component ϵ' yields a semicircle whose coordinates are determined by the above three parameters [4]. The frequency dependence of the permittivity of normal alcohols has been shown to be more complex involving at least two relaxation processes [9]. A similar plot of the data results in more than one semicircle, the radius of each semicircle decreasing as the frequency range increases. In the case of normal alcohols [9], the slowest relaxation process, which is characterized by values of τ_D which are in the order of 0.1 ns, has been attributed to the formation and breakup of hydrogen-bonded clusters. The second process which has a much shorter relaxation time is ascribed to the diffusional rotation of monomers. This process is most directly related to dielectric relaxation for aprotic solvents in which hydrogen bonding is absent. Finally, a very fast relaxation process is attributed to rotation of the hydroxyl group around the C–O bond in the alcohol.

Another solvent which exhibits non-Debye behaviour, but for quite different reasons, is propylene carbonate [10,11]. This molecule has a large dipole moment (4.98 Debyes $\equiv 1.66 \times 10^{-29}$ $\not{C}$m) and strong dipole–dipole interactions relative to most non-aqueous solvents used in electrochemistry [12]. On the basis of molecular orbital calculations [13], it is concluded that the molecule has significant dipole moments perpendicular to two principal axes but a negligible one perpendicular to the heterocyclic ring. In general, an asymmetrical top molecule such as propylene carbonate would be expected to exhibit three distinct molecular relaxation times corresponding to reorientation about its three principal inertial axes [10]. Presumably, because one of the three components of the principal dipole vector is negligible, only two relaxation processes are seen experimentally [10,11]. In fact, all aprotic solvent molecules considered here are asymmetrical and depart from the point dipole model to some extent or other. However, analysis of the dielectric relaxation data to determine the necessary parameters seems to have been carried out only in the case of propylene carbonate.

According to the theory of solvent dynamical effects on electron transfer reactions [14,19], the pre-exponential factor of the rate constant for electron transfer depends on the longitudinal solvent relaxation time, τ_L, in the case of adiabatic reactions. For aprotic solvents with one relaxation process, τ_L is easily estimated from the parameters, τ_D, ϵ_0 and ϵ_s [16–18]. However, in the case of solvents with more than one relaxation process, the relationship between τ_L and the experimental relaxation parameters is much more complex [20], the solvent friction being predicted to depend on frequency. For weakly adiabatic reactions in the alcohols, the effective value of τ_L is close to that one would calculate on the basis of the parameters of the second relaxation process alone [7,20]. This result explains why electron transfer processes in the alcohols and propylene carbonate appear anomalously fast with respect to those in Debye solvents [5–8]. McManis and Weaver [21]

examined the consequences of Hynes's theory for τ_L [20] using different models for non-Debye solvents and showed that the rate enhancement observed for homogeneous electron transfer reactions involving various metallocene systems in methanol. ethanol and propylene carbonate [8] could be estimated using this model.

When one reads the current literature on electron transfer theory, one is left not only with the impression that significant new developments have occurred during the last few years, but also that the subject of solvent effects in these reactions is exceedingly complex. The purpose of the present paper is to reexamine these effects with respect to simple and more complex solvents, and to demonstrate that the nature of these effects are such that they can be easily examined and understood qualitatively on the basis of existing experimental data. Examination of protic solvents is limited to the alcohols for which extensive dielectric relaxation data have been reported [22.23]. Unfortunately, similar data at high frequencies are not available for the protic amides so that results in these systems are not considered here.

THEORY

As a result of recent theoretical developments [14-9] it is now recognized that the solvent may affect the rate of electron transfer in at least two ways. On the basis of Marcus theory [24], the magnitude of the outer sphere contribution to the Gibbs energy of activation ΔG^* depends on the dielectric properties of the solvent. In addition, for adiabatic reactions in which the outer sphere contribution to ΔG^* is much larger than due to inner sphere reorganization, the preexponential factor of the electron transfer rate constant depends on the dynamical properties of the solvent [14-19]. As a result, for reactions in which the inner sphere contribution to ΔG^* is solvent independent, the electron transfer rate constant may be expressed by the equation

$$k_r = A\tau_L^{-\alpha} \exp\left[-(\Delta G_{is}^* + \Delta G_{os}^*)/RT \right] \tag{1}$$

where A is the solvent independent part of the pre-exponential factor. α, a fraction between 0 and 1, ΔG_{is}^*, the inner sphere contribution to the Gibbs energy of activation and ΔG_{os}^*, the outer sphere contribution. The fraction α is a function of reaction adiabaticity and the relative contributions of the inner and outer sphere reorganizational energies [19]. If the reaction is weakly adiabatic, and/ or ΔG_{is}^* is large relative to ΔG_{os}^*, α approaches zero. On the other hand, if the reaction is strongly adiabatic and the contribution of ΔG_{is}^* is negligible, α approaches unity.

The important parameter determining the solvent dependence of the pre-exponential factor is the longitudinal relaxation time, τ_L. In the case of a simple Debye solvent it is defined as

$$\tau_L = (\epsilon_\infty/\epsilon_s)\tau_D \tag{2}$$

It falls in the range from 0.1 to 10 ps, a typical fast solvent being acetonitrile ($\tau_L = 0.2$ ps) and a slow one, hexamethylphosphoramide ($\tau_L = 8.8$ ps). Application

4

of eqn. (1) to electron transfer kinetic data in aprotic solvents has met with considerable success for both homogeneous and heterogeneous systems [3].

In the case of a solvent with multiple relaxation processes, the dielectric response may be expressed as

$$E(\omega) = \sum_i f_i (1 - j\omega\tau_i)^{-1} \qquad (3)$$

where f_i is the fractional contribution associated with relaxation time τ_i and ω is the angular frequency. In the case of alcohols, this expression becomes

omega missing

$$E(\omega) = \frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{f_1}{1 + j\tau_1} + \frac{f_2}{1 + j\omega\tau_2} + \frac{f_3}{1 + j\omega\tau_3} \qquad (4)$$

where

$$\downarrow$$
$$\omega$$

$$f_1 = \frac{\epsilon_s - \epsilon_{mw}}{\epsilon_s - \epsilon_\infty} \qquad (5)$$

$$f_2 = \frac{\epsilon_{mw} - \epsilon_{ir}}{\epsilon_s - \epsilon_\infty} \qquad (6)$$

$$f_3 = \frac{\epsilon_{ir} - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} \qquad (7)$$

ϵ_{mw}, ϵ_{ir}, and ϵ_∞ are the limiting dielectric constants defining the end of the first, second and third relaxation processes, respectively. In Laplace space, the dielectric response is written as

$$\hat{E}(s) = \sum_i f_i (1 + s\tau_i)^{-1} \qquad (8)$$

Hynes [20] has shown that under the above circumstances, the longitudinal relaxation time in Laplace space is given by

$$\hat{\tau}_L(s) = \left[\sum_i f_i (1 + s\tau_i)^{-1} \right]^{-1} (\epsilon_\infty/\epsilon_s) \sum_i f_i \tau_i (1 + s\tau_i)^{-1} \qquad (9)$$

error in text—should be $\geq$

Thus, it is clear that τ_L depends on frequency. In the case that only two relaxation processes are important ($f_i = 0$, $i \not\leq 3$), equation (9) becomes [20]

$$\geq$$

$$\hat{\tau}_L(s) = \tau_{L\infty} + \frac{\tau_{Lo} - \tau_{L\infty}}{1 + s\tau'} \qquad (10)$$

where

$$\tau_{Lo} = (\epsilon_\infty/\epsilon_s)(f_1\tau_1 + f_2\tau_2) \qquad (11)$$

$$\tau_{L\infty} = \frac{\epsilon_\infty}{\epsilon_s} \left[\frac{f_1}{\tau_1} + \frac{f_2}{\tau_2} \right]^{-1} \qquad (12)$$

and

$$\tau' = f_1\tau_2 + f_2\tau_1 \qquad (13)$$

Here, τ_{Lo} is the low frequency value of τ_L which is governed by the average value of the longitudinal time, and $\tau_{L\infty}$ is the high frequency value which is dominated by the faster relaxation time. The transition between these extremes is determined by the time τ'. Thus, in effect, the rate constant for solvent relaxation is time dependent, the exact nature of the time dependence depending on the characteristics of the reaction in which solvent relaxation is involved [20]. Hynes considered solvent dynamical effects for strongly and weakly adiabatic, and nonadiabatic reaction systems, and demonstrated that for weakly adiabatic systems τ_L is close to $\tau_{L\infty}$.

In assessing the above results, one should keep in mind that the fractions f_1, f_2 and f_3 defined above only apply to the pure solvent. For low molar mass straight chain alcohols, f_1 is close to 0.9 so that one would expect the contribution of the first relaxation process to predominate. However, the second relaxation time is at least twenty times smaller than the first so that, in the case of $\tau_{L\infty}$, the effect of the second relaxation is predominant. In the vicinity of the solute involved in the electron transfer reaction, solvent structure can be quite different than in the pure solvent. For instance, large organic solutes can promote hydrogen bonding so that the fraction f_1 approaches unity. Under these circumstances the expressions for both τ_{Lo} and $\tau_{L\infty}$ become

$$\tau_{L1} = (\epsilon_\infty/\epsilon_s)\tau_1 \tag{14}$$

where τ_{L1} is the limiting value of the longitudinal relaxation time in a solvent with no monomers ($f_2 = 0$). This limiting case for alcohols was considered previously by Sumi and Marcus [25]. On the other hand, if the hydrogen-bonded solvent structure is broken up near the solute such that the fraction f_2 approaches unity, the appropriate limiting form for the longitudinal relaxation time is

$$\tau_{L2} = (\epsilon_\infty/\epsilon_{mw})\tau_2 \tag{15}$$

In writing this equation, the distinction between ϵ_∞ and ϵ_{ir} has been dropped, it being assumed that the fraction f_3 is negligible. Equation (15) was used by Chase and Hunt [26] to account for solvation times of electrons in alcohols. Because a single electron is so small its disruptive influence on the surrounding solvent is very great, and the influence of clusters on the longitudinal relaxation time can be neglected.. As will be shown below, values of $\tau_{L\infty}$ calculated on the basis of parameters for the pure solvent fall between τ_{L1} and τ_{L2} but lie closer to τ_{L2} for low molecular weight straight chain alcohols. Since the parameters used to examine solvent effects in Debye solvents and those based on the properties of the pure solvent, it is appropriate that the properties of non-Debye solvents be examined with respect to τ_{Lo} and $\tau_{L\infty}$.

RESULTS

Dielectric relaxation data for the alcohols

A summary of the dielectric parameters for the alcohols considered in this study is given in Table 1. Although numerous studies of the frequency dependence of the

TABLE 1

Dielectric data for non-Debye solvents

Solvent	Dispersion region	Low frequency dielectric constant ϵ_0	High frequency dielectric constant ϵ_∞	Debye relaxation time τ_D/ps	Refractive index n
methanol	1	32.65	5.51	49.8	1.3265
	2	5.51	2.0	1.1 [28]	
ethanol	1	24.34	4.42	172	1.3594
	2	4.42	2.1	6.5 [29]	
1-propanol	1	20.58	3.65	418	1.3837
	2	3.65	2.2	19.1 [27]	
1-butanol	1	17.20	3.43	517	1.3973
	2	3.43	2.2	25.5 [9]	
propylene carbonate	1	64.9	9.3	41.2	1.4209
	2	9.3	5.3	14.7	

dielectric properties of these systems have been carried out [22,23], results from different laboratories are often in disagreement. This is partially due to differences in the models used to interpret the data but also reflects the difficulty in obtaining precise results at high frequencies. For this reason, the data relating to the second relaxation process are considerably less precise than those for the first. Castner et al. [27] presented an excellent summary of data for low molar mass alcohols, and their values are given for the first relaxation process of the alcohols. Values of the second relaxation time came from various sources as noted in the table. The value of the limiting dielectric constant for the second relaxation process, $\epsilon_{2\infty}$ was assumed to be close to 2 for all alcohols considered on the basis of data reported by Garg and Smyth [9], and Bottreau et al. [30]. In the case of propylene carbonate, the parameters cited are those obtained by Barthel and Feuerlein [11].

Values of the limiting longitudinal relaxation times τ_{Lo} and $\tau_{L\infty}$ (eqns. 11 and 12) defined by Hynes [20] for a solvent with two relaxation processes are summarized for the five solvents considered here in Table 2. In the case of propylene

TABLE 2

Longitudinal relaxation times for non-Debye solvents

Solvent	Low and high frequency limits		Value for clusters in alcohols	Value for monomers in alcohols
	τ_{Lo}/ps	$\tau_{L\infty}/ps$	τ_{L1}/ps	τ_{L2}/ps
methanol	12.7	0.5	3.1	0.4
ethanol	13.4	4.1	14.9	3.1
1-propanol	41.3	16.9	44.7	11.5
1-butanol	60.9	25.6	66.1	16.4
propylene carbonate	3.2	3.0		

carbonate the difference between these two quantities is negligible. However, for the alcohols the value of τ_{Lo} is always significantly larger than that of τ_{Lx}. Values of τ_{L1} and τ_{L2} defined in eqns. (14) and (15), respectively, are also given for the alcohols. The difference between τ_{Lo} and τ_{Lx} illustrates the problems that were experienced in interpreting solvent effects for the alcohols in earlier work [5–8]. If the estimate of the longitudinal relaxation time is based on τ_{Lo} or τ_{L1}, then the predicted pre-exponential factor for the rate constant is too small by approximately an order of magnitude. This question is now examined in more detail.

Kinetic data for electron transfer

As pointed out above, the behaviour of redox systems in non-Debye solvents is anomalous with respect to that in Debye solvents, the rate constants for electron transfer being higher than expected on the basis of the relaxation parameters for the first relaxation process. As an example, we consider first the kinetic data for the electrooxidation of 1.4-diaminobenzene (DAB/DAB$^+$) at a Pt electrode obtained by Opallo [6] in twelve different organic solvents. A plot of the logarithm of the standard rate constant for this reaction k_s, against the logarithm of τ_L for solvents
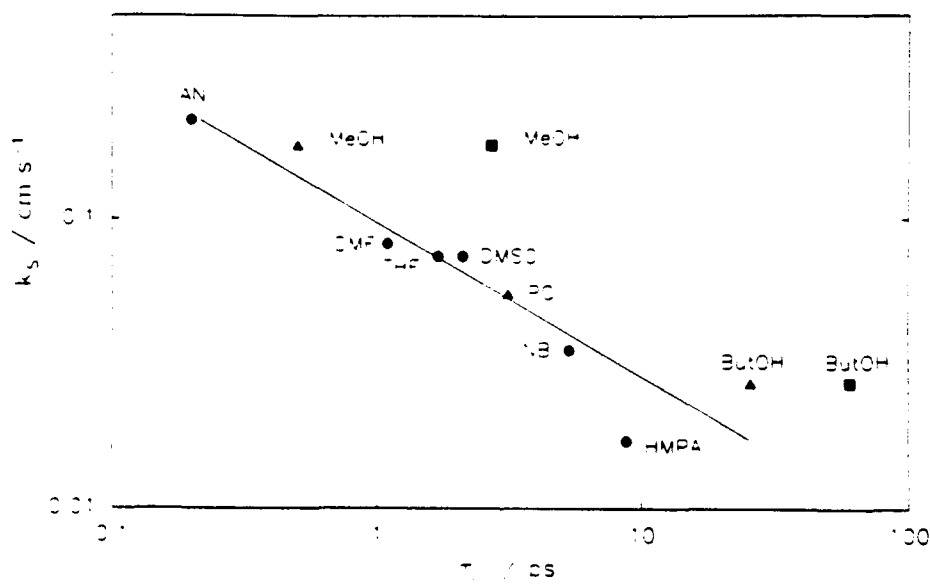

Fig. 1. Plot of the logarithm of the rate constant for electrooxidation of 1.4-diaminobenzene at a Pt electrode in nine solvents against the logarithm of the solvent's longitudinal relaxation time. Data points designated by a circle are for Debye solvents; those designated with a triangle are for non-Debye solvents using $\tau_{L\infty}$ (eqn. 12) and those with a square, for the same solvents using τ_{Lo} (eqn. 11). The symbols for the solvents are as follows: AN, acetonitrile; ButOH, n-butanol; DMF, dimethylformamide; DMSO, dimethylsulfoxide; HMPA, hexamethylphosphoramide; MeOH methanol; NB, nitrobenzene; PC, propylene carbonate; THF, tetrahydrofuran.
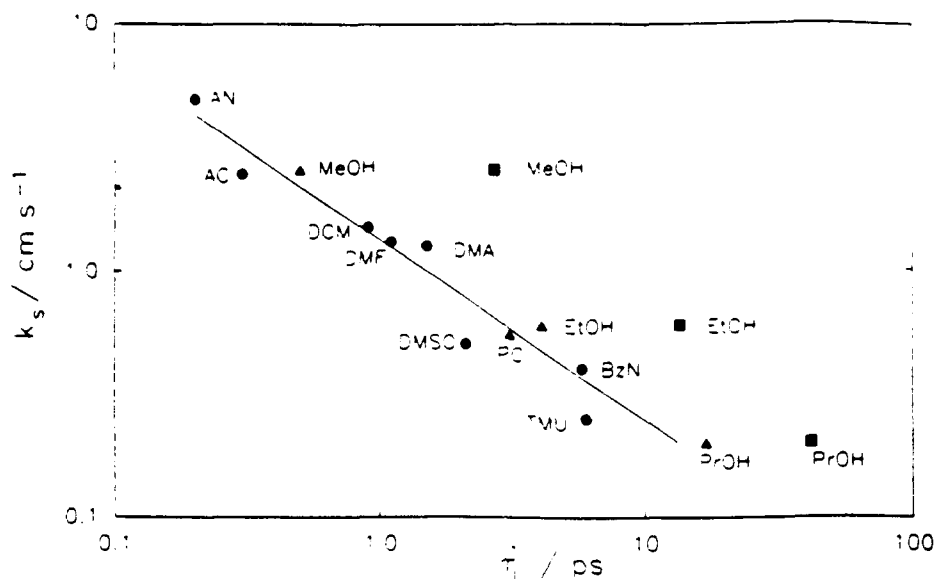
Fig. 2. Plot of the logarithm of the rate constant for the electroreduction of cobaltacenium cation at a Hg electrode in twelve solvents against the logarithm of the solvent's longitudinal relaxation time. The designation of the data points and the symbols for the solvents are those given in the legend to Fig. 1 with the following additional solvents: AC, acetone; BzN, benzonitrile; DCM, dichloromethane; DMA, dimethylacetamide; EtOH, ethanol; PrOH, n-propanol; TMU, tetramethylurea.

for which dielectric relaxation data are available is presented in Fig. 1. In the case of the alcohols, the data were plotted using the limiting values of τ_L based on Hynes's theory, namely, τ_{Lo} and $\tau_{L\infty}$. For propylene carbonate, τ_L was assumed to be 3.1 ps on the basis of the data of Barthel and Feuerlein [11]. It is immediately clear that the data obtained in alcohols solutions correlate well with those in aprotic solvents when τ_L is assumed to equal $\tau_{L\infty}$. The correlation coefficient for the best straight line through these points is 0.940, the slope being -0.5. It is emphasized that the plot shown in Fig. 1 ignores the fact that k_s depends on the nature of the solvent through the solvent dependence of ΔG_{os}^*. If the latter dependence is considerably smaller, a reasonable estimate of the parameter α can be obtained from the slope of the plot provided there are no trends in ΔG_{os}^* which fortuitously follow τ_L. In a previous analysis of these data using a three parameter least squares fit, the estimate of α was 0.6 ± 0.1 on the basis of data in the aprotic solvents only [3].

Data for the electroreduction of cobaltacenium cation (COB$^+$/COB) at Hg in eleven non-aqueous solvents are shown in Fig. 2. One sees clearly again for this system that the data for the alcohols correlate well with those in aprotic solvents when τ_L is estimated on the basis of the high frequency value, $\tau_{L\infty}$. The correlation coefficient for the best straight line is 0.973 and the value of the slope, -0.7. These data confirm that the appropriate value of τ_L for the alcohols is the high frequency

limit. If one uses $\tau_{L:}$ instead of $\tau_{L\infty}$ for the alcohols, a slightly better fit to the data is obtained. This suggests that solvent structure is somewhat different near the reactant, the concentration of monomers being higher. The estimate of the parameter α in the present case is significantly smaller than that obtained previously [3], which was 1.0 ± 0.1. This difference is attributed to the fact that the previous analysis which considers the variation in ΔG_{os}^* with solvent included propylene carbonate with parameters appropriate for a Debye solvent. When this analysis is repeated using data for Debye solvents only, the revised estimate of α is 0.9 ± 0.1, a result which is in better agreement with that based on the approximate analysis from Fig. 2. It follows that the COB^+/COB system is only weakly adiabatic as a heterogeneous process.

When the parameter α is known, the solvent dependence of the Gibbs energy of activation may be examined by correcting the logarithm of the rate constant for the solvent dependence of the pre-exponential factor. Thus, on the basis of eq. (1), one may write

$$\ln k_s + \alpha \ln \tau_L = a - g\gamma \tag{16}$$

where

$$a = \ln A - \Delta G_{is}^*/RT \tag{17}$$

and

$$\Delta G_{os}^*/RT = g\gamma \tag{18}$$

γ is the permittivity parameter defined by the equation

$$\gamma = \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \tag{19}$$

and g is defined for heterogeneous reactions as

$$g = \frac{N_o e^2}{32\pi\epsilon_0}\left(\frac{1}{a} - \frac{1}{R_e}\right) \tag{20}$$

In the above equations, ϵ_{op} is the optical dielectric constant, N_o, Avogadro's constant, e, the electronic charge, a, the radius of the reactant represented as a sphere, R_e, its distance from its image in the conducting electrode, and ϵ_0, the permittivity of free space. The above expression for ΔG_{os}^* which is based on Marcus's theory for electron transfer [24] has been questioned in recent theoretical work by Kornyshev and coworkers [31–33]. It was pointed out that ΔG_{os}^* should be less than predicted by eqn (18) due to spatial dispersion of the dielectric permittivity near the electrode [32]. Furthermore, the effect of penetration of the field into the metal electrode should be considered in estimating ΔG_{os}^*. It is clear that estimates of ΔG_{os}^* considering these effects are very model dependent [32,33]. The effect of dielectric saturation near the reactant is examined here using a simple *but arbitrary* alternative estimate of ΔG_{os}^* based on the static dielectric constant of the solvent

that would be observed in the absence of the first relaxation process. namely, ϵ_{mw}. Thus. in the case of non-Debye solvents. ΔG_{os}^{*} is estimated using the equation

$$\Delta G_{os}^{*}/RT = g\gamma'$$ (21)

where

$$\gamma' = \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_{mw}}$$ (22)

This estimate of ΔG_{os}^{*} is obviously smaller than that based on eqn. (18) and would be appropriate in the alcohols if the solvent near the reactant behaves essentially as monomers without the additional structure due to hydrogen bonding.

A plot of the kinetic data for heterogeneous electron transfer in the COB^{+}/COB system [7] according to eqn. (16) and assuming that $\alpha = 0.9$ is shown in Fig. 3. It is apparent that a reasonable fit to the experimental data is obtained for the aprotic solvents when the permittivity parameter is defined on the basis of eqn. (19). Analysis of the slope and intercept gives reasonable values for the size–distance and pre-exponential parameters as discussed earlier [3]. However, when the data for the alcohol solvents are added. it is clear that the correlation between $\ln k_s + \alpha \ln \tau_L$
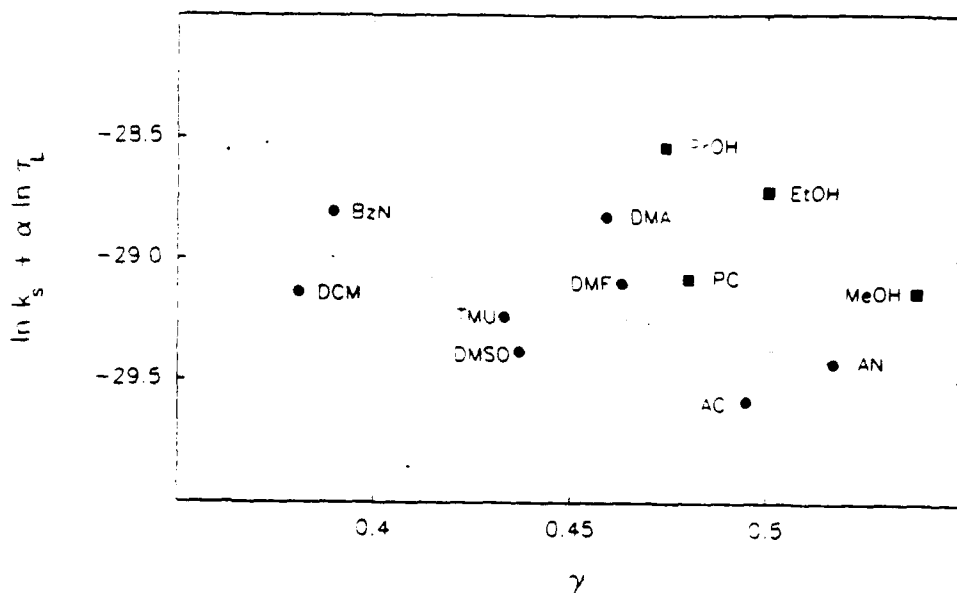

Fig. 3. Plot of the logarithm of the standard rate constant for reduction of COB^{+} corrected for variation in the longitudinal relaxation time of the solvent, $\ln k_s + \alpha \ln \tau_L$, against the permittivity parameter for the solvent γ. Data for Debye solvents are designated (●) and those for non-Debye solvents, (■). The symbols for the solvents are given in the legends to Figs. 1 and 2. The dotted line shows the correlation based on Debye solvents only. The units of k_s are ms^{-1} and of τ_L, s.
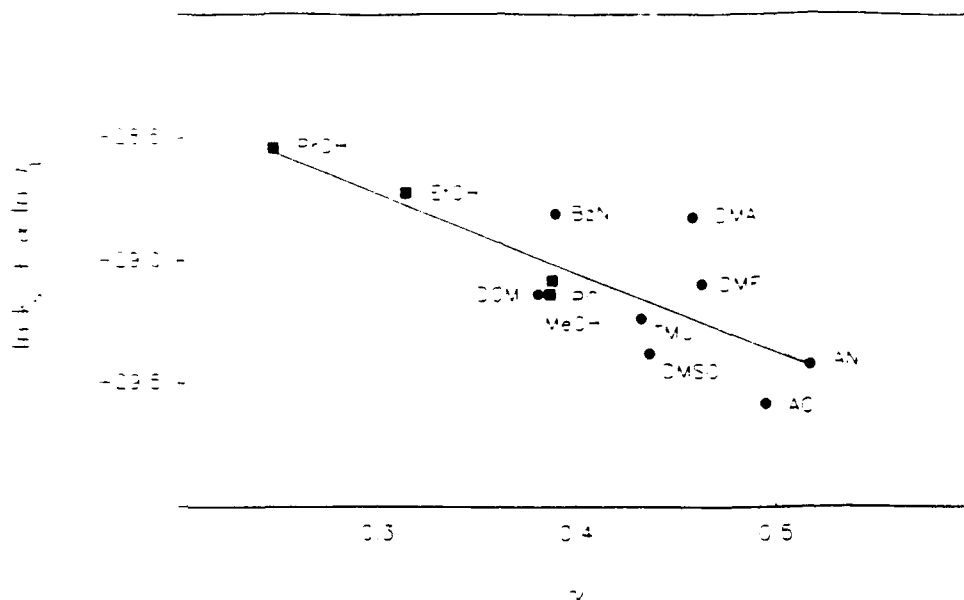
Fig. 4. Plot of the logarithm of the standard rate constant for reduction of COB⁻ corrected for variation in the longitudinal relaxation time of the solvent, In $k_s + \alpha$ In τ_L, against the revised permittivity parameter γ' for the solvent (eqn. 22). Data for Debye solvents are designated (●) and those for non-Debye solvents, (■). The symbols for the solvents are given in the legends to Figs. 1 and 2. The full line shows the correlation based on all the solvents, and the dotted line, on the Debye solvents only. The units of k_s are ms⁻¹ and of τ_L, s.

and . is lost, and that one cannot make reasonable estimates of the kinetic parameters. A plot of the same data but with the permittivity parameter γ' defined according to eq. (22) for the alcohols and propylene carbonate is shown in Fig. 4. It is clear that the correlation is restored, the parameters for the straight line drawn with twelve solvents being insignificantly different that those obtained on the basis of eight aprotic solvents. In the case of the alcohols, this result suggests that the reactant in this system is solvated by monomers, and that the local dielectric constant is lower than the bulk value.

A plot of data for homogeneous electron transfer in the COB⁺/COB system [8] according to eqn. (16) is shown in Fig. 5. As is apparent, a very good correlation between In $k + \alpha$ In τ_L and γ' is observed with the datum for benzonitrile being significantly off the best straight line. The value of α for this system was assumed to be 0.7 on the basis of our previous work [3]. If one uses γ for the non-Debye solvents, the correlation no longer holds because the points for methanol, ethanol and propylene carbonate are then shifted well to the right of the best line drawn with Debye solvents alone. It is also probably true that benzonitrile is a non-Debye solvent on the basis of its shape and the location of the polar group in the molecule [34]. If it behaves like propylene carbonate, it is probable that the parameters from a
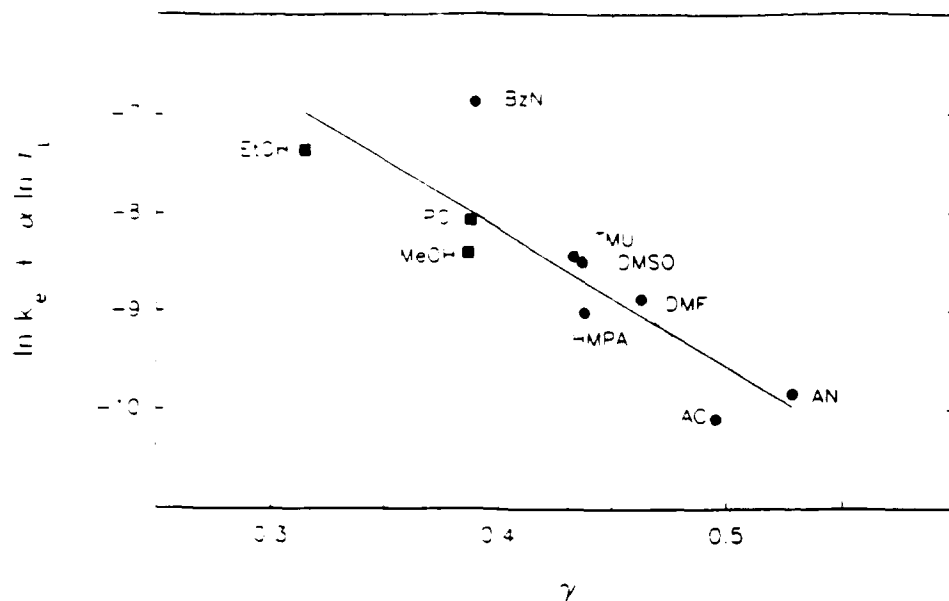
Fig. 5. Plot of the logarithm of the exchange rate constant for electron transfer in the COB/COB^+ system corrected for variation in the longitudinal relaxation time of the solvent, $\ln k + \ln \tau_L$, against the revised permittivity parameter γ' for the solvent (eqn. 22). Data for the Debye solvents are designated (●) and those for non-Debye solvents, (■). The symbols for the solvents are given in the legends to Figs. 1 and 2. The full line shows the correlation based on all the solvents, and the dotted line, on the Debye solvents only. The units of k are $m^3 \, mol^{-1} \, s^{-1}$ and those of τ_L, s.

more detailed description of the dielectric relaxation process would result in an improved fit of this datum with the others shown in Fig. 5.

A summary of the parameters from fits of experimental data to eqn. (16) is given in Table 3. It is clear that the quality of the fits is not excellent but certainly acceptable. The scatter in the plots shown in Figs. 4 and 5 is likely due to errors in

TABLE 3

Kinetic parameters for electron transfer reactions analyzed according to eqn. 16.

	α	g/RT	n	r	
Homogeneous reactions					
Cobaltacene (0/+) [8]	0.7	-2.6 ± 1.2	14.0 ± 2.9	10	0.866
Heterogeneous reactions					
Cobaltacenium (+/0) [7]	0.9	-27.7 ± 0.3	3.6 ± 0.6	12	0.896
Diaminobenzene (0/+) [6]	0.6	-22.2 ± 0.3	3.0 ± 0.8	9	0.824
Phenothiazene (0/+) [5]	0.7	-23.3 ± 0.3	5.8 ± 1.1	10	0.877

$\alpha \qquad a \qquad g/RT \qquad n \qquad r$

the kinetic data. Furthermore. additional error is introduced due to the uncertainty in the values of τ_L both for Debye [3] and non-Debye solvents. It is also likely that solvents such as benzonitrile, and nitrobenzene should be treated as non-Debye liquids similar to propylene carbonate, but unfortunately the dielectric relaxation data are not sufficiently extensive to permit calculation of the necessary parameters.

If one compares the values of the parameter g with those obtained earlier for systems where $\alpha = 1$, it is clear that the present results are smaller. This is due to the fact that the dependence of the pre-exponential factor on ΔG_{os}^* which was considered previously has been ignored in the present analysis. In the case of the process of homogeneous electron transfer in the COB^-/COB system which has been treated here as weakly adiabatic ($\alpha = 0.7$), the value of g is quite reasonable and gives a size–distance parameter of 1.0 nm. Assuming that this corresponds to twice the molecular radius a, one obtains an estimate of a (0.5 nm) which is close to that found from crystallographic data (0.37 nm). In the case of the heterogeneous electron transfer reactions, the estimates of the size–distance parameter are considerably larger than the molecular radius a. This parameter is estimated to be equal to "a" when imaging effects in the electrode are negligible. ($R_e = \infty$ in eq. 20). On the basis of the present results R_e is finite, and the values of ΔG_{os}^* considerably less than those that would be estimated assuming $R_e = \infty$.

No attempt is made here to analyze the significance of the intercept parameter "a" reported in Table 3. Since the parameter α is less than one for the systems considered, the dimensions of the pre-exponential factor are such that it is not easily interpreted in terms of existing theories. However, it is clear that the values of the other pre-exponential parameters depend greatly on the value assumed for α.

DISCUSSION

On the basis of the above analysis it is clear that the solvent dependence of the pre-exponential factor for adiabatic and weakly adiabatic electron transfer reactions can be rationalized in the case of non-Debye solvents using the high frequency estimate of the longitudinal relaxation time from the model developed by Hynes [20]. Accordingly, the anomalously fast rate constants found in the alcohols, protic amides, and propylene carbonate can be attributed to the dominating influence of a faster relaxation process in the solvent. The role of solvent relaxation is easily demonstrated on the basis of plots of the logarithm of the electron transfer rate constant against the logarithm of the longitudinal relaxation time [5,6]. Furthermore, if the magnitude of ΔG_{is}^* is known, the slope of such a plot can give some qualitative indication of the degree of reaction adiabaticity but it cannot be used to estimate the parameter α because of possible fortuitous trends in the solvent dependence of ΔG_{os}^* for the group of solvents considered. Estimation of α should be based on a multiparameter least-squares fit so that the solvent dependence of the pre-exponential factor may be separated from that of the exponential term [3]. However, it is clear for the systems considered here that the solvent dependence of the pre-exponential factor predominates. Thus, precise estimates of τ_L must be

available from the literature data if one is going to make a reasonable analysis of the solvent dependence of ΔG_{os}^{*}.

As far as ΔG_{os}^{*} is concerned, the striking result obtained here is that non-Debye solvents behave similarly to Debye solvents if ΔG_{os}^{*} is estimated on the basis of the dielectric parameters characterizing the faster relaxation process, that is, on γ' (eqn. 22). As a result the estimates of ΔG_{os}^{*} are much smaller for these systems than suggested by the more conventional interpretation of the Marcus model for electron transfer [24]. In the case of the alcohols, the present results suggest that the reactants are solvated predominantly by solvent monomers rather than clusters. Some support for the conclusion that the Marcus model may overestimate ΔG_{os}^{*} is available from the theoretical work of Kornyshev et al. [31–33] but this treatment does not distinguish between Debye and non-Debye solvents, and the estimates of ΔG_{os}^{*} are very dependent on the details of the model. It should also be emphasized that the degree of solvent-structure disruption is expected to depend on the charge and size of the reactant. Thus, the effects seen here for the metallocenes may well different for other reacting systems.

In earlier work [2], we implicitly assumed that the parameter α is unity for all systems considered. This assumption allowed for provisional estimates of the size–distance parameter g, and, in cases where ΔG_{is}^{*} was known, the prefactor, κK_p. A more complete analysis presented later [3] outlined a statistical strategy for estimating α, and for delineating the circumstances where certain limiting absolute rate expressions were applicable in the determination of g and κK_p. The three parameter regression analysis was limited to aprotic solvents where the relaxation times and permittivity parameters are better defined. In this paper, we have presented a method of determining the appropriate relaxation times in solvents that exhibit multiple relaxation behaviour. We also show that the permittivity parameters used in the calculation of ΔG_{os}^{*} must be consistent with those used in the calculation of τ_L from τ_D. In the case of the alcohols, the fact that the kinetic data correlate with the relaxation times and dielectric constants associated with the second dispersion region implies that the local dielectric constant is not ϵ_s but ϵ_{mw}.

The authors feel obliged to address recent criticism by Phelps et al. [33] directed at our earlier work [2]. In a strongly worded footnote, these authors object to our *alleged* conclusion that the electronic transmission coefficient κ is very much less than unity in the COB^+/COB system. In fact, we *did not* discuss the parameter κ alone, but rather the product κK_p where K_p is the equilibrium constant for precursor complex formation [35]. This product was found to be much lower than theory predicts. Indeed, since the analysis employed in ref. 2 implicitly assumes that $\alpha = 1$ and therefore that $\kappa = 1$, a conclusion that $\kappa \ll 1$ would be inconsistent. However, a low value of κK_p is neither inconsistent with the assumptions engendered in the analysis, nor is it physically unreasonable. We also stated that the parameter κK_p should be solvent sensitive due to the fact that the distance between the reactant and the interface is expected to depend on solvent size. Therefore, the criticism made by these authors of our earlier work is unwarranted in our opinion. We feel strongly that the analysis used here and earlier [2,3] provides insight into the

role of the solvent in the electron transfer process on the basis of the fewest possible assumptions, and permits a deeper understanding of the role of the solvent in electron transfer processes.

ACKNOWLEDGEMENT

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